

FORM PTO-1390 (Modified)
(REV 11-98)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES

JMYT-233US

DESIGNATED/ELECTED OFFICE (DO/EO/US)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)

CONCERNING A FILING UNDER 35 U.S.C. 371

To Be Assigned 09/763981

INTERNATIONAL APPLICATION NO.

PCT/GB99/02803

INTERNATIONAL FILING DATE

25 August 1999 (25.08.99)

PRIORITY DATE CLAIMED

28 August 1998 (28.08.98)

TITLE OF INVENTION

SENSING GASEOUS SUBSTANCES USING METAL COMPLEXES

APPLICANT(S) FOR DO/EO/US

ELSONE, Amanda Maria

SLADE, Elizabeth

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). (UNEXECUTED)
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☐ Other items or information:

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) 09/463981		INTERNATIONAL APPLICATION NO. PCT/GB99/02803		ATTORNEY'S DOCKET NUMBER JMYT-233US	
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21. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO	\$970.00	CALCULATIONS PTO USE ONLY	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO	\$840.00		
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	\$690.00		
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4)	\$670.00		
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)	\$96.00		

ENTER APPROPRIATE BASIC FEE AMOUNT =

Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).	<input type="checkbox"/> 20 <input type="checkbox"/> 30	\$0.00
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CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	9 - 20 =	0	x \$18.00		\$0.00
Independent claims	2 - 3 =	0	x \$80.00		\$0.00
Multiple Dependent Claims (check if applicable).					\$0.00
TOTAL OF ABOVE CALCULATIONS =					\$860.00

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). ☐

\$0.00

SUBTOTAL =

\$860.00

Processing fee of **\$130.00** for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). ☐ 20 ☐ 30

\$0.00

TOTAL NATIONAL FEE =

\$860.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☐

\$0.00

TOTAL FEES ENCLOSED =

\$860.00

	Amount to be refunded	\$
	charged	\$

☒ A check in the amount of **\$860.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.

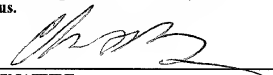
☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **18-0350** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Christopher R. Lewis
RATNER & PRESTIA
 Suite 301
 One Westlakes, Berwyn
 P.O. Box 980
 Valley Forge, PA 19482-0980

Phone: (610) 407-0700
 Facsimile: (610) 407-0701



SIGNATURE

Christopher R. Lewis

NAME

36,201

REGISTRATION NUMBER

February 28, 2001

DATE

FORM PTO-1390 (Modified) (REV 11-98)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER JMYT-233US	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) 09/763,981	
INTERNATIONAL APPLICATION NO. PCT/GB99/02803		INTERNATIONAL FILING DATE 25 August 1999 (25.08.99)		PRIORITY DATE CLAIMED 28 August 1998 (28.08.98)	
TITLE OF INVENTION SENSING GASEOUS SUBSTANCES USING METAL COMPLEXES					
APPLICANT(S) FOR DO/EO/US ELSONE, Amanda Maria SLADE, Elizabeth					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> 1. <input type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input checked="" type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). 4. <input type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7. <input type="checkbox"/> A copy of the International Search Report (PCT/ISA/210). 8. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 9. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 10. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). 11. <input type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). 12. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)). <p>Items 13 to 20 below concern document(s) or information included:</p> <ol style="list-style-type: none"> 13. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 14. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 15. <input type="checkbox"/> A FIRST preliminary amendment. 16. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 17. <input type="checkbox"/> A substitute specification. 18. <input type="checkbox"/> A change of power of attorney and/or address letter. 19. <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail 20. <input checked="" type="checkbox"/> Other items or information: <div style="border: 1px solid black; padding: 5px; margin-top: 5px;"> <p>A copy of the Notification of Missing Requirements and Notification of a Defective Oath or Declaration</p> </div>					

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) 09/763,981	INTERNATIONAL APPLICATION NO. PCT/GB99/02803	ATTORNEY'S DOCKET NUMBER JMYT-233US
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21. The following fees are submitted:				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :					
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO				\$970.00	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO				\$840.00	
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<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)				\$96.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$0.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30				\$130.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	- 20 =	0	x \$18.00	\$0.00	
Independent claims	- 3 =	0	x \$80.00	\$0.00	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$130.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). <input type="checkbox"/>				\$0.00	
SUBTOTAL =				\$130.00	
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30 +				\$0.00	
TOTAL NATIONAL FEE =				\$130.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input checked="" type="checkbox"/>				\$40.00	
TOTAL FEES ENCLOSED =				\$170.00	
134 130.00 OP				Amount to be refunded:	\$
				charged	\$

- ☒ A check in the amount of **\$170.00** to cover the above fees is enclosed.
- ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.
- ☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **18-0350** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

**Christopher R. Lewis
RATNER & PRESTIA
Suite 301
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Facsimile: (610) 407-0701**

SIGNATURE

Christopher R. Lewis

NAME

36,201

REGISTRATION NUMBER

May 23, 2001

DATE

09/763981

JC03 Rec'd PCT/PTO 28 FEB 2001

CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10)Applicant(s): **ELSOME, Amanda Maria and SLADE, Elizabeth**

Docket No.

JMYT-233US

Serial No. To Be Assigned	Filing Date Herewith	Examiner	Group Art Unit
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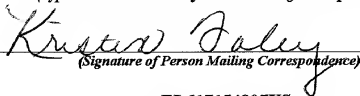
Invention: **SENSING GASEOUS SUBSTANCES USING METAL COMPLEXES**

I hereby certify that the following correspondence:

U.S. National Phase Application w/Form PTO-1390, and all documents listed therein,

(Identify type of correspondence)

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: The Assistant Commissioner for Patents, Washington, D.C. 20231

February 28, 2001*(Date)***Kristen Foley***(Typed or Printed Name of Person Mailing Correspondence)*

*(Signature of Person Mailing Correspondence)***EL617154807US***("Express Mail" Mailing Label Number)***Note: Each paper must have its own certificate of mailing.**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Amanda Maria Elsome et al. : Art Unit:
Serial No.: To be Assigned : Examiner:
Filed: : Herewith :
FOR: : SENSING GASEOUS SUBSTANCES :
USING METAL COMPLEXES :

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

Box PCT

S I R :

Prior to examination, pleased amend the above-identified application
as follows.

IN THE SPECIFICATION:

On page 1, after the title, please insert the following sentence:

-- This application is the U.S. national-phase application of PCT
International Application No. PCT/GB99/02803.--

IN THE DRAWINGS:

Please add the enclosed informal drawing, Figures 1, 2, 3, 4, and 5.

IN THE CLAIMS:

Please delete claim 8 and amend claims 2, 3, 4, and 6, as follows:

- 1 2. (Amended) A sensor according to claim 1, wherein the gaseous
2 substance is selected from the group consisting of at least one of a sulphur-
3 containing compound, [and/or] a nitrogen-containing compound, [and/or] an

1 alcohol-containing compound, [and/or] a carbonyl-containing compound, [and/or]
2 and a phosphorous-containing compound.

3 3. (Amended) A sensor according to claim 1 [or 2], wherein the
4 metal complex is a metal complexed with a chromophore or fluorophore.

5 4. (Amended) A sensor according to claim 1, [2 or 3,] wherein the
6 metal complex is immobilised in a film or incorporated into or into part of a
7 packaging material.

8 6. (Amended) A sensor according to [any one of the preceding
9 claims] claim 1, wherein the metal complex is a palladium-fluorophore complex.

REMARKS

The Assistant Commissioner is hereby authorized to charge payment
to Deposit Account No. 18-0350 of any fees associated with this communication.

Respectfully submitted,

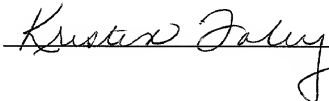


Christopher R. Lewis, Reg. No. 36,201
Paul F. Prestia, Reg. No. 23,031
Attorneys for Applicants

CRL/bgd
Dated: February 28, 2001
Suite 301
1 Westlakes, Berwyn
P.O. Box 980
Valley Forge, PA 19482
(610) 407-0700

EXPRESS MAIL Mailing Label Number: EL617154807US
Date of Deposit: February 28, 2001

I hereby certify that this paper and fee are being deposited, under 37 C.F.R. § 1.10 and with sufficient postage, using the "Express Mail Post Office to Addressee" service of the United States Postal Service on the date indicated above and that the deposit is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.



Kristen Foley

SENSING GASEOUS SUBSTANCES USING METAL COMPLEXES

The present invention concerns improvements in sensors, and more particularly concerns improvements in sensors for detecting microbial food spoilage.

Microbial spoilage of foods is a major concern to food producers, retailers and consumers. Consumers may perceive spoilage as a deterioration in taste, appearance, smell and/or texture, and there are clear health risks too. Currently, there is no direct in-pack measurement of food spoilage. Producers/retailers use "best before" and "use by" dates as an indication of food quality and safety. However, these methods are merely a prediction of food quality and are not a real measurement of food quality.

Food can spoil by a number of processes, including lipid oxidation, enzymatic degradation and microbial growth. The relative importance of these food spoilage processes vary from food to food, according to its constitution, handling history, and other factors. Microbial growth, however, is a major spoilage factor.

There are many methods currently used to determine food quality, *eg* organoleptic tests, standard microbiological techniques and spectroscopic analysis. None of these techniques are currently suitable for use in-pack, and may have other disadvantages such as long evaluation times and sample destruction. Accordingly, there is a need for a technique which can continuously monitor food quality in-pack, from packaging to consumption.

It has been proposed to use a fluorophore chelated with manganese for the quantitative detection of S-containing pesticides (Int. J. Environ. Chem. (1971), 1 (2), 99-111). Also, the fluorophore calcein has been described as being complexed with palladium with added zinc, to detect organo-sulphur drug residue compounds in chromatography techniques (J. Chromat. 442 (1988) 459-463) in which the compounds are spotted onto thin layer chromatography plates.

It has also been suggested that the concentration of sulphur-containing vapours from dry-cured hams could be detected by the quenching of fluorescence in tetractylammonium

fluorescein mercuric acetate (Sensors and Actuators B 38-39 (1997) 390-394). However, such a sensor compound would never be acceptable for use inside food packaging. Further, we believe that it would be more desirable for retailers to be able to detect spoilage by detecting the appearance of fluorescence or the appearance of a chromophore than by detecting the quenching of fluorescence.

Microbial growth on food and chemical degradation tends to result in the formation of volatile spoilage products. We have invented a product and method which utilises such spoilage products within the pack to sense food spoilage. Although the present invention will be described hereinafter with particular reference to food spoilage, it should be understood that its principles may be more widely applied. Thus it is contemplated that the invention may be applied to detecting the opening or the compromise of sterile packaging of instruments, dressings or drugs, in the microelectronics industry, as an aid to the quality assurance process in food factories, and in security packaging for papers, securities, banknotes, and other valuables.

The present invention provides a sensor for detecting food spoilage or the opening or compromise of packaging, comprising a metal co-ordinated complex immobilised in or on a substrate, which complex is capable of releasing a detectable component by the preferential binding of a gaseous substance to the metal of said complex. The complex may be, for example, a metal complexed with a chromophore or fluorophore, which undergoes ligand exchange with sulphur compounds (*eg* sulphides) or nitrogen compounds (*eg* amines), thus releasing the chromophore or fluorophore to indicate spoilage. Other gases relevant to the present invention contain alcohol or carbonyl groups or contain phosphorus.

Desirably, the complex is immobilised in the form of a film, which may be formed by printing, casting, roller application, brushing, spraying or like techniques, a composition comprising the complex onto the internal surface of the food package. In another embodiment, the complex is incorporated into, or into part of, a food packaging material itself. The invention therefore also provides such a composition for application onto food packaging, comprising the complex, an immobilising resin and a liquid vehicle. The system

used for immobilising the complex may also retain and immobilise the chromophore or fluorophore. If required it is possible to incorporate some form of barrier layer or coating which is permeable to the food spoilage products but not to the indicator molecule or metal compounds.

5

A variety of metals may be used to form the complex, and include especially palladium, platinum, ruthenium or iron, but other metals may be considered, such as copper, nickel, zinc, gold, the rare earth metals, cobalt, iridium, titanium and vanadium.

10

Some retailers may desire that the complex releases a fluorophore which does not show any appreciable colour change under normal shop lighting, but fluoresces strongly when excited by non-visible light such as UV. This permits the retailer to scan packages, eg by a portable UV lamp, and remove those that show release of the fluorophore caused by food spoilage products. For other areas of use, release of a chromophore, giving a visible colour change, may be more desirable. A variation on release of a fluorophore is the reaction of the complex to cause a shift in the position of an emission peak. This may be sufficient to be visible by eye when the fluorophore is excited, but the invention also encompasses the detection of such a shift by an instrument. It is to be understood that the term "chromophore" as used in the present invention includes compounds which exhibit phosphorescence.

15

20

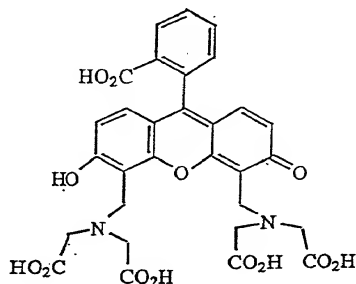
25

The release of the chromophore or fluorophore is desirably not specific to any type or species of microorganism. The invention is believed to be sufficiently flexible to permit the development of a variety of sensors, either which indicate directly the level of microorganism growth or which switch "on" at a given level; for example a strip of sensors may indicate increasing levels of contamination up to a danger level.

30

Desirably, the complex also may be designed for particular uses, and to achieve particular results. For example, a particular palladium-fluorophore complex exhibits very much faster kinetics for fluorophore release than the corresponding platinum-fluorophore complex. According to the intended use and the preferred kinetics either, or both,

complexes may be used to yield particular preferred results. The complexing ligand is not itself critical providing it is released from the metal in the appropriate time-frame, and provides on reaction with spoilage products the desired fluorescence or colour change characteristics. A preferred ligand is Fluorexon, of general formula



This may be reacted with $\text{Na}_2[\text{PdCl}_4]$ to yield a Pd-Fluorexon complex which is pink in colour but which fluoresces strongly when the ligand is released. The Fluorexon molecule can itself be modified so that it is no longer water soluble, but is soluble in lipids or organic solvents, for example by using a non-co-ordinating counterion or by changes in functional groups, as is well known to the skilled chemist. The preparation of such a palladium complex is described in more detail in the following Example.

Other palladium complexes may be considered for use in the present invention are known from the literature, for example palladium dializarin red, $(\text{NBu}_4)_2[\text{PdAlizarin}_2]$ and the palladium complex of alizarin complexone. Generally, the complex may be any suitable complex of a dye, a complexone, a Schiff base, or could be a rare earth polyamino carboxylate. Particular complexing fluorophores to be considered in addition to Fluorexon are known *per se*, and include a number of compounds commercially available, such as fluorescein isothiocyanate, fluorescein, fluoresceinamine, calcein blue, "Fura 2", quinizarin, alizarin complexone, alizarin red and alizarin, isoccein, "Quin 2" and 4,4-dihydroxy-azobenzene 3,3-dicarboxylic acid, disodium salt.

The presently preferred Pd-Fluorexon complex may be dissolved in an aqueous PVA solution, to form a composition which can be applied to plastics packaging materials to yield a water-insoluble film. It is envisaged that other such compositions, with other metal complexes, may be established by trial and error, and it is convenient to use generally available ink-forming technology. Such an ink may be applied to the inner surface of a package, or printed or otherwise applied onto a label for insertion into a package. Such inks or compositions may contain other components, including particularly one or more of driers, plasticisers, fillers, surfactants and pigments. In addition to labels to be packaged inside packaging, the invention includes adhesive labels, decals and the like.

Alternatively, incorporation of the complex into the packaging material may be considered, providing that when so incorporated, there is sufficient permeability to cause the complex to release the desired detectable component.

The present invention will now be described by way of example only.

EXAMPLE 1

A. Preparation of Solution of Pd:Fluorexon

4'5'-Bis(N,N-bis(carboxymethyl)aminomethyl fluorescein (0.1g , $1.6 \times 10\text{m}^{-4}$) and $\text{Na}_2(\text{PdCl}_4)$ (0.12g , $3.2 \times 10^{-4}\text{m}$) were suspended in H_2O (90cm^3) and heated under reflux for 30 minutes. The suspension was filtered whilst warm, resulting in a red/pink solution. A tarry dark red/brown residue was removed during filtration. The resulting solution is approximately 1.6 m M .

B. Preparation of Solution of Pd:Fluorexon in PVA

4g of the solution prepared in A above was added to a commercial 6% PVA (16g , Rhone Poulenc 25-140 Rhodoviol) in H_2O solution, and mixed in a high shear mixer for 5 minutes.

C. Production of Film

0.5cm³ of the mixture resulting from B above was drawn into a film on a polyester film sheet (Mylar) using a K-bar size 3, and left to dry at room temperature. A smooth film coating was formed, pale pink in colour.

D. Tests for Spoilage Products from Meat

A variety of tests were carried out on samples of fresh minced beef and chicken purchased from a local butcher. The samples were sub-divided and left with the existing natural flora. The samples were either refrigerated at 4°C or stored at room temperature in closed vessels in which was located a 1cm x 1cm label cut from the film produced as in C above.

E. Fluorescence Testing

E(i) Initial tests were carried out on a Fluorexon solution in water (a) and the Fluorexon solution immobilised in a film produced from 10% PVA in analogous manner to C above (b), and fluorescence peaks were determined. These are plotted in accompanying Figure 1.

It can be seen that there is a distinct fluorescence peak at about 520nm for the solution and at about 530nm for the film, demonstrating a slight shift because of the matrix of the film.

E(ii) Samples of the Pd:F solution prepared in A above were taken. One was retained as a control (a) and other samples were admixed with 10⁻⁶ M diethylamine. Fluorescence was measured at various times and the fluorescence spectra are plotted on accompanying Figure 2. It was readily seen that there is an increasing intensity with time, demonstrating the release of fluorescent ligand from the complex. Similar results have been obtained when the diethylamine was replaced with the amino-acid cysteine.

E(iii) The fluorescence of the labels used in the tests described in D above was established. In the case of the meat stored in the refrigerator, the fluorescence plots are

shown in Figures 3 and 4 at 24 hours and at 168 hours (seven days) respectively. It is to be noted that in Figure 4 the Y scale is very much expanded in comparison to Figure 3. A very small peak is shown for the film exposed to chicken breast (a) in Figure 3, but there is no significant fluorescence from the film exposed to minced beef (b). A control of film sample stored over sterile water (c) is shown for comparison. However, by 168 hours, there has been a dramatic increase in intensity in fluorescence in both cases. Both sample looked and smelled "spoilt" by this stage.

In the case of the meat stored at room temperature for 24 hours, the label fluorescence plots are shown in Figure 5. Both chicken breast (a) and minced beef (b) show dramatic peaks at about 550nm. The control (c) of a label over sterile water does not show any corresponding peak. Although the intensity of the fluorescence from these meat labels is not so great as that resulting from seven days in the refrigerator, it is clear that the spoilage process has begun and that the Pd complex is being affected by spoilage products to release the fluorophore.

ART 34 ANDT

CLAIMS

1. A sensor for detecting food spoilage products within food packaging or the opening or compromise of packaging, comprising a metal co-ordinated complex immobilised in or on a substrate, which complex is capable of releasing a detectable component by the preferential binding of a gaseous substance to the metal of said complex.
2. A sensor according to claim 1, wherein the gaseous substance is a sulphur- and/or nitrogen- and/or alcohol- and/or carbonyl- and/or phosphorus-containing compound.
3. A sensor according to claim 1 or 2, wherein the metal complex is a metal complexed with a chromophore or fluorophore.
4. A sensor according to claim 1, 2 or 3, wherein the metal complex is immobilised in a film or incorporated into or into part of a packaging material.
5. A sensor according to claim 4, wherein said film is applied to a label retained inside packaging or to the interior surface of a portion of a package.
6. A sensor according to any one of the preceding claims, wherein the metal complex is a palladium-fluorophore complex.
7. A sensor according to claim 6, wherein the complex is palladium-Fluorexon.
8. A sensor substantially as hereinbefore described.
9. A method of detecting the degradation of the contents of food packaging, or the opening or compromise of a package, comprising inserting into or applying to said package or incorporating into a portion of the interior surface of said package, a metal co-ordinated complex which is capable of releasing a detectable component by preferential binding of a gaseous substance to the metal atom(s) of said complex.

10. A method according to claim 9, wherein food spoilage is detected by the release of a fluorophore or a chromophore from a metal complex.

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Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled
SENSING GASEOUS SUBSTANCES USING METAL COMPLEXES,

the specification of which is attached hereto unless the following box is checked:

☒ was filed on February 28, 2001 as
 United States Application Number or PCT International Application Number 09/763,981
 and was amended on February 28, 2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below by checking the box, any foreign application for patent or inventor's certificate, or PCT international application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

Priority Not Claimed

9818766.9

Great Britain

August 28, 1998

(Number)

(Country)

(Day/Month/Year Filed)

☐

(Number)

(Country)

(Day/Month/Year Filed)

☐

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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